

# PATENT SPECIFICATION

NO DRAWINGS

1.055,723

1.055,723



Date of Application and filing Complete Specification: March 20, 1964.  
No. 11941/64.

Application made in France (No. 928982) on March 22, 1963.

Complete Specification Published: Jan. 18, 1967.

© Crown Copyright 1967.

Index at acceptance: —C5 E B2K1

Int. Cl.: —C 07 c 5/10

## COMPLETE SPECIFICATION

### Cycloalkane Hydrocarbons and Method for their Production

We, CHARBONNAGES DE FRANCE, a Public Institution organized under the laws of the French Republic of 9 avenue Percier, Paris, Seine, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Cycloalkane hydrocarbons are used commercially especially as solvents and heat-exchanger liquids. They are also advantageous as jet fuels by reason of their high combustion heat per unit weight and volume, their low viscosity, their low freezing point and the low radiation of their flame.

The present invention relates to a new method of preparation of hydrocarbons rich in naphthenes and in particular of mixtures completely free from olefin hydrocarbons and in which the content of fully saturated hydrocarbons is at least 95% and preferably greater than 98%, the said method starting with raw materials which are essentially aromatic such as fractions of coal tars, hydrogenates of coal or materials of petroleum origin rich in polynuclear aromatic hydrocarbons.

The invention also relates to the products obtained by this method.

It has already been proposed to hydrogenate such fractions at high temperatures over catalysts which are resistant to sulphur. Under these conditions, the hydrogenation reaction is not complete and is accompanied by a high degree of cracking.

This cracking can be reduced and the saturation can be increased by observing certain conditions: high pressure and large flow of hydrogen, very strict control of the temperature, reduction of space velocity. British Patent No. 935,712 belonging to the present

Applicant constitutes one example of such an improved method.

However, even under the best conditions, it is hardly possible to obtain more than 95% of fully-saturated hydrocarbons from a raw material constituted essentially by polycyclic aromatic hydrocarbons unless excessive flow-rates of hydrogen and contact times are employed. On the other hand, it is known that it is possible to obtain higher rates of saturation by proceeding to a second operation of hydrogenation on catalysts constituted by metals of the eighth group of the periodic classification of elements, such as nickel, platinum and palladium. However, these catalysts are very sensitive to impurities, and especially to sulphur compounds. Under penalty of a rapid poisoning of the catalyst, it is thus essential to desulphurize the charge very carefully in the first hydrogenation operation and to eliminate entirely the sulphuretted hydrogen formed by expansion or by washing. The hydrogen which must then be injected into the second stage should be free from these impurities which are harmful to the catalyst.

It has now been found that this second hydrogenation can be carried out in the presence of a catalyst which is resistant to sulphur, of the same type as that employed in the first stage of hydrogenation, while obtaining a substantially complete saturation of the charge and avoiding the costly operations of expansion of the mixture and re-injection of fresh hydrogen, by respecting new conditions which are defined below.

The method according to the invention comprises the introduction of an essentially aromatic raw material such as a fraction of coal tar, a hydrogenate of coal or a material of petroleum origin rich in polynuclear aromatic hydrocarbons into a first stage of hydrogenation.

[Price 4s. 6d.]

tion on a strongly-hydrogenating catalyst comprising a sulphide of tungsten and/or nickel on alumina, under a pressure of hydrogen equal to or exceeding 100 bars, the upper limit of the reaction temperature being 450°C, the cooling of the product passing out of this first stage and its admission into a second stage of hydrogenation over a catalyst comprising a sulphide of tungsten and/or nickel on alumina at a pressure of hydrogen exceeding 100 bars, the temperature of the said admission and the other conditions of reaction being determined in such manner that the upper limit of the temperature in the second stage is less than the upper limit of the temperature in the first stage and is between 260° and 400°C and preferably between 300° and 380°C.

In accordance with another characteristic feature, the total quantity of hydrogen introduced into the reaction stages is more than 3,000 litres measured at standard temperature and pressure per kg. of original material.

Excess hydrogen may be recycled to the first reaction stage in which the raw product is treated. This recycled hydrogen may be subjected to washing under pressure by means of various solvents in order to eliminate the gaseous hydrocarbons formed.

The raw product can advantageously be washed by means of selective solvents such as methanol, so as to eliminate the oxygen, sulphur and nitrogen products which it is not desired to hydrogenate.

According to an advantageous characteristic the final product is distilled, preferably in the absence of oxygen.

The use of a sulphide catalyst in the two reaction stages enables the hydrogen of the first stage to be utilized in the second. An addition of fresh hydrogen in the second stage will not generally be necessary, and in the cases where such an addition would appear to be preferable, impure hydrogen may be injected.

A particular advantage of the method according to the invention is that it comprises only a single flow system for gas and liquid and does not require either purification or other operation except cooling, between the two reaction stages.

It is quite clear that without departing from the scope of the invention it is possible to employ more than one reactor for each hydrogenation stage, or on the other hand to utilize only a single reactor for the two stages, with two different temperature zones, the cooling of the second zone being obtained by any method such as an internal exchanger, or injection of cold hydrogen.

By combining the conditions specified above, it is possible to obtain a conversion rate of more than 95%, that is to say to reduce the content of aromatic and hydro-aromatic hydro-

carbons to less than 5% and preferably less than 2%.

Other advantages and particular features of the invention will be brought out in the examples given below by way of explanation only and not in any limitative sense.

#### EXAMPLE I

The product treated in this example was a creosote oil having the following characteristics:

—Elementary analysis: C=91.4%; H=6.3%; O=1.0%; N=0.5%; S=0.8%.

—Distillation:

10% distilled over below 208°C;

50% distilled over below 293°C;

90% distilled over below 370°C.

The analysis shows that the main constituents of this oil are naphthalene, the mono- and dimethyl-naphthalenes, acenaphthene, dibenzo-furan, fluorene, phenanthrene, anthracene.

A mixture of this oil and hydrogen under a pressure of 200 bars in which the hydrogen was at a partial pressure of at least 180 bars, the flow-rates by weight being in the ratio of 6/1, was pre-heated to 340°C and then sent into a reactor containing, per kg. of raw product introduced per hour, 2.06 litres of a commercial catalyst composed of nickel sulphide and tungsten sulphide deposited on alumina and containing 6% by weight of nickel and 19% by weight of tungsten. The surface area of the catalyst was 140 sq.m., per gram. The temperature of the gases in this reactor was always kept below 440°C by the injection at various levels of 0.34 kg. of cold hydrogen per kg. of charge.

The mixture passing out of the first reactor was cooled down to 320°C and sent into a second reactor containing 0.38 litre of the same commercial catalyst per kg. of raw product introduced per hour. The partial pressure of the hydrogen in this stage was at least 190 bars. The gases leaving this second reactor at about 330°C were cooled and the hydrogenate was separated from the gas in a separator, washed with water and then topped under nitrogen to remove the fractions which distil below 150°C.

The product obtained was a colourless liquid having a density of 0.884 at 20°C and a solidification point less than 60°C. It does not contain aromatic hydrocarbons which can be detected by the method of displacement chromatography on silica gel. Its thermal stability was very good. In particular, it easily passed the test JP.6 for reactor fuels in accordance with the American Standard Mil-F-25.656 A, and even a more severe test under the Standard Mil-J-25.656 B.

Tests carried out in the C.F.R. Fuel Coker:

—Pre-heater: temperature 204°C, coloration 0; filter; temperature 260°C, pres-

sure drop 1.3 mm/Hg in 300 minutes for a flow-rate of 2.7 kg/hr (Mil-F-25.656A).  
 —Pre-heater: temperature 218°C, coloration 0; filter; temperature 274°C, pressure drop 2.5 mm/Hg in 300 minutes (Mil-F-25.555 B).

#### EXAMPLE 2

By way of comparison, the second reactor was eliminated. After washing and distillation to separate the heads, there was obtained a colourless product having a density of 0.887 and still containing 10.5% of aromatic and hydro-aromatic hydrocarbons. This product does not pass the JP.6 test.

#### EXAMPLE 3

The conditions of Example 1 were reproduced with the exception that the temperature at the outlet of the second reactor was 400°C. Under these conditions, the content of aromatic and hydro-aromatic hydrocarbons was 2.5%.

There is thus an advantage in the second reactor being at a temperature less than 400°C.

#### EXAMPLE 4

A mixture of the creosote oil and hydrogen with flow-rates by weight in the ratio of 6/1 at a pressure of 200 bars in which the hydrogen was at a partial pressure of at least 180 bars was pre-heated to 340°C and then sent into a reactor containing 1.40 litre per kg. of product and per hour of the same catalyst as in the preceding Examples. The maintenance of the temperature below 440°C necessitated the addition of 0.3 kg. of cold hydrogen per kg. of oil. The partial pressure of hydrogen in this stage was at least 190 bars. The gases passing out of the reactor were cooled to 360°C and introduced into a second reactor containing, per kg. of charge and per hour, 0.87 litre of the same catalyst. The reaction mixture thus brought to the vicinity of 350°C by the exothermal nature of the reaction was then cooled and partly expanded in a separator in which was carried out the separation of the gases and the fractions which distil at less than 150°C. The remaining colourless liquid had a content of residual aromatic and hydro-aromatic hydrocarbons of 1%, it easily passed the test JP.6 for thermal stability (Mil-F-25.656 A).

#### EXAMPLE 5

As the liberation of heat is particularly high at the beginning of the reaction, the first hydrogenation in this Example was carried out in two successive reactors, which permits easier control of the temperature.

The creosote oil of Example 1 was injected with 0.55 kg. per hr. of charge of a gas containing 90% of hydrogen at a pressure of 220 bars. This gas was derived partly

from re-cycling of hydrogen and partly by the addition of fresh hydrogen. The mixture, pre-heated to 350°C was sent into a reactor containing 0.80 litre of the same commercial catalyst as in Example 1, per kg. of charge introduced per hour. The partial pressure of the hydrogen in the mixture was at least 195 bars. The temperature in this reactor was kept below 420°C by the injection at various points of 0.20 kg. of cold gas per kg. of charge.

The mixture passing out of this first reactor was cooled in an exchanger and sent into a second reactor containing 0.75 litre per kg. of charge and per hour of the same catalyst, at a temperature chosen in such manner that the liberating of heat due to the reaction did not increase the temperature of the gases leaving this reactor beyond 420°C. At this stage the partial pressure of the hydrogen was at least 190 bars. These gases were cooled in an exchanger and sent into a third reactor containing 0.75 litre per kg. of charge and per hour of the same catalyst, at a temperature such that their temperature did not rise above 380°C by the effect of the liberation of heat.

The effluent of this third reactor was cooled, washed with water, the liquid product obtained separated from the gas and the water, distilled so as to remove the fractions passing over below 150°C and then passed over bleaching earth.

The gas containing excess hydrogen was sent to the inlet of the first reactor after washing with oil when so required.

The product obtained did not contain any aromatic hydrocarbons.

#### EXAMPLE 6

The charge was a chrysene oil having the following characteristics:

—Distillation: 5% point—320°C  
 50% point—400°C  
 95% point—480°C

—Main constituents:

phenanthrene	10.4%
fluoranthene	10.10%
pyrene	11.70%
chrysene	15.70%

This charge was introduced into the installation at the same time as a re-cycled oil, the respective flow-rates being in the ratio of 100 to 43. A part of this mixture was pre-heated to 380°C with 0.01 kg. per kg. of the total charge of hydrogen at a partial pressure of 400 bars, and then sent into a reactor containing 0.60 litre per kg. of charge introduced per hour of a commercial catalyst based on tungsten and nickel sulphides on alumina. The catalyst contained 4.5% of nickel and 9.5% of tungsten. Its surface area was 194 sq. m. per gram. The remainder of the charge and 0.6 kg. of hydrogen per kg. of charge were introduced

directly into the reactor at various points chosen in such manner that the temperature did not exceed 450°C.

5 The mixture passing out of this first reactor at about 440°C was put into contact in a vaporizer with 0.40 kg. of hydrogen per kg. of charge, heated to a temperature such that 70% of the products were vaporized. The residue was re-cycled to the inlet of the first reactor.

10 The mixture of vapor and hydrogen in which the partial pressure of the hydrogen was of the order of 400 bars, was introduced after cooling to 350°C into a second reactor containing 0.50 litre of the catalyst of Example 1 per kg. of charge and per hour and thus brought to 390°C. It was cooled and sent into a separator in which the separation of the liquids was effected, and was then washed and distilled in order to eliminate about 3.5 parts of product which pass over below 150°C. Per 100 parts of charge there are obtained 52 parts of a fraction 150°—310°C which can be used as a high energy fuel, and 39.5 parts of a fraction 25 distilling above 310°C. This fraction may be employed in various ways. The content of hydro-aromatic hydrocarbons of the mixture before distillation was 3.2%.

#### 30 WHAT WE CLAIM IS:—

1. A method of preparation of hydrocarbons rich in cycloalkane hydrocarbons and in particular of mixtures completely free from olefin hydrocarbons and in which the content of fully-saturated hydrocarbons is at least 95% and preferably exceeds 98%, the said method comprising the introduction of an essentially aromatic raw material such as a fraction of coal tar, a hydrogenate of coal or a material of petroleum origin rich in polynuclear aromatic hydrocarbons into a first stage of hydrogenation on a strongly hydrogenating catalyst comprising a sulphide of tungsten and/or nickel on alumina, under a pressure of hydrogen equal to or exceeding 100 bars, the upper limit of the reaction

temperature being 450°C, the cooling of the product passing out of this first stage and its admission into a second stage of hydrogenation over a catalyst comprising a sulphide of tungsten and/or nickel on alumina at a pressure of hydrogen exceeding 100 bars the temperature of the said admission and the other conditions of reaction being determined in such manner that the upper limit of the temperature in the second stage is less than the upper limit of the temperature in the first stage and is between 260° and 400°C and preferably between 300° and 380°C.

2. A method in accordance with Claim 1, in which the total quantity of hydrogen introduced into the reaction stages is more than 3,000 litres measured at standard temperature and pressure per kg. of original material.

3. A method in accordance with Claim 1 or 2, in which excess hydrogen is recycled to the first reaction stage in which the raw product is treated; the said excess hydrogen being subjected to a washing under pressure by means of various solvents in order to eliminate the gaseous hydrocarbons formed.

4. A method in accordance with any one of Claims 1 to 3, in which the raw product is washed by means of selective solvents such as methanol, so as to eliminate the oxygen, sulphur and nitrogen products which it is not desired to hydrogenate.

5. The products obtained by carrying into effect the method in accordance with any one of Claims 1 to 4.

6. The products in accordance with Claim 5, in which the final product is distilled, preferably in the absence of oxygen.

7. A method of preparation of fully-saturated hydrocarbons, substantially as hereinbefore described and as illustrated in the foregoing Examples 1 and 3 to 6.

PAGE, WHITE & FARRER,  
Chartered Patent Agents,  
27, Chancery Lane,  
London, W.C.2.  
Agents for the Applicants.